

Temperature-Programmed Reduction and Temperature-Resolved Sorption Studies of Strong Metal-Support Interaction in Supported Palladium Catalysts

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Palladium catalysts on various supports were prepared for strong metal-support interaction (SMSI) studies. The reduction and hydrogen sorption for these catalysts were investigated by a combination of temperature-programmed reduction and temperature-resolved sorption techniques. Palladium was found to be reduced at temperatures lower than 200°C. Spillover of hydrogen from Pd to supports occurred at higher temperatures. Hydrogen treatment at high temperatures also induced SMSI and sintering. The extent of spillover, sintering, and SMSI are support-dependent. The absorption of hydrogen into bulk palladium was also suppressed by SMSI. Under the same reduction conditions, the sintering of supported palladium catalysts follows the trend Pd/C > Pd/TiO₂ > Pd/Al₂O₃ > Pd/SiO₂. © 1985 Academic Press, Inc.

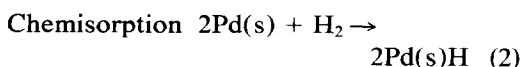
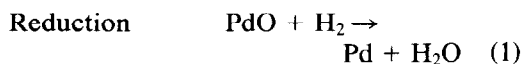
INTRODUCTION

Reduction is an activation step in the synthesis of metallic catalysts. It is also a necessary pretreatment for chemisorption measurements when the dispersion of metallic catalysts is investigated. Treatment at low temperatures may result in an incomplete reduction. High temperatures, however, can cause both sintering and strong metal-support interaction (SMSI) for the dispersed metal. Deciding the optimum reduction conditions is therefore an art in catalyst characterization and synthesis.

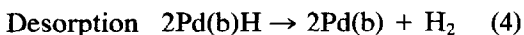
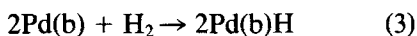
SMSI is a phenomenon reported and named by Tauster *et al.* (1, 2) for supported metallic catalysts. This interaction comes from a reduction at elevated temperatures which reduces the cations of the support to an oxidation state lower than its original state. The most striking consequence of this interaction is a suppression of H₂ and CO chemisorptions on the supported metals. A subsequent calcination may convert the reduced cation to its normal oxidation state and relieve the SMSI situation.

The percentage of exposed metal (*D*, widely referred to as dispersion) is an im-

portant indication of the quality of supported metallic catalysts. Hydrogen chemisorption is a generally used method to estimate the exposed percentage of supported noble metal catalysts (3). Palladium differs from other noble metals in interaction with hydrogen because, in addition to chemisorption, it absorbs hydrogen into the bulk (4). This absorption interferes with the chemisorption and may cause an error in the determined dispersion of palladium catalysts. Many methods have been suggested in the literature to resolve this interference. In our laboratory, Pd/Al₂O₃ catalysts of various dispersions, have been studied in a 10% H₂/Ar flow system (5). The consumption of H₂ by these catalysts as a function of the reactor temperature was determined using a thermal conductivity detector. On increasing the temperature gradually from -90 to 400°C, calcined Pd/Al₂O₃ exhibited the following reactions at 0.1 atm partial pressure of hydrogen:



Absorption



and



where Pd(s) denotes the surface palladium atom and Pd(b) is the atom in the bulk of the metal crystallites. On cooling the catalysts from 400°C to room temperature in the flow system, hydrogen chemisorption reoccurred at high temperatures and hydrogen absorption into the bulk palladium took place at low temperatures (around 90°C) during this cooling process. By measuring the area ratio of these two sorption peaks, the dispersion of the Pd/Al₂O₃ catalysts may be determined by this "temperature-resolved sorption" (TRS) phenomenon according to the equation

$$D = A_c / (A_c + 2.8A_a), \quad (1)$$

where A_c is the peak area from the chemisorption (Reaction 2) and A_a denotes that from the absorption (Reaction 3).

This same TRS method has also been successfully applied to determine the dispersion of Pd/SiO₂ catalysts. On application to other supported palladium catalysts (such as Pd/C), this method was less reproducible. The irreproducibility may be caused by SMSI which reduces the reactivity of palladium toward hydrogen sorptions. Since TRS is a very convenient method for monitoring sorption properties of active palladium catalysts, we were interested in the use of this technique to investigate the possible SMSI of supported palladium.

EXPERIMENTAL

Catalyst Preparation

Sample A (1% Pd/SiO₂). This catalyst was prepared by the cation exchange

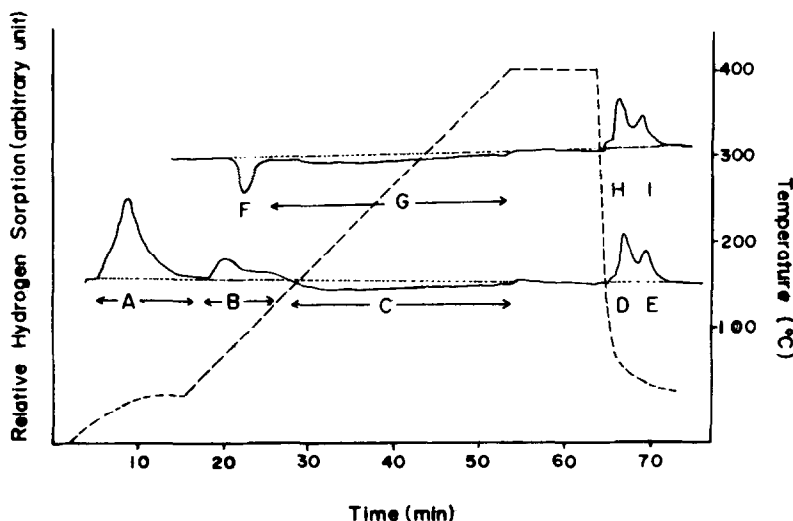


FIG. 1. TPR and TRS spectra Pd/SiO₂ (sample A), showing two temperature increasing–decreasing cycles in H₂/Ar at 0.1 atm H₂ partial pressure (see text). The dashed line indicates the profile of the temperature treatment and the difference between the solid lines and the dotted lines (the baselines) represents the consumption (positive peaks) and desorption (negative peaks) of H₂ by the sample. The first temperature cycle produces peaks A to E. Peak A comes from incomplete Reactions (1) to (3) (see text) at room temperature. These reactions become complete at higher temperatures, and merge with Reaction (4) to generate peak B. Peaks C and G are broad negative peaks from Reaction (5). Peaks D and H come from Reaction (2) while peaks E and I result from Reaction (3). Peak F which occurs around 90°C illustrates Reaction (4).

method. PdCl_2 was dissolved in concentrated ammonia to form $\text{Pd}(\text{NH}_3)_4^{2+}$ complex cations. These cations were exchanged with the protons on SiO_2 powders (Kieselgel 60 from Merck) in concentrated ammonia solution.

Sample B (Pd/TiO₂). This catalyst was prepared by the impregnation technique. PdCl_2 from Merck was dissolved with concentrated HCl. The H_2PdCl_4 formed was mixed with acetone and subsequently impregnated into TiO_2 supports (synthesized in the laboratory of Professor M.-T. Lee of the National Taiwan University).

Sample C (1% Pd/Al₂O₃). This catalyst was prepared by the anion exchange method. PdCl_4^{2-} anions from $\text{PdCl}_2\text{-HCl}$ were exchanged with OH^- groups on alumina (from Merck) in acidic aqueous solution ($\text{pH} = 2.0 \pm 0.2$).

Sample D (5% Pd/C). This catalyst was prepared by cation exchange between $\text{Pd}(\text{NH}_3)_4^{2+}$ ions with protons on activated carbon (reagent grade from Riedel-Dehaen) at $\text{pH} = 11.0 \pm 0.4$.

The above samples were subsequently dried at 110°C and calcined at 400°C (sample D was calcined at 200°C). The palladium contents of these samples were measured by neutron activation analysis.

Method

Precalcined samples were inserted into the reactor of our TPR system, which is described elsewhere (5). The reactor was held at -70°C before a stream of 10% H_2/Ar gas mixture at 1 atm was passed through to displace the air in the reactor. The time profiles of the H_2 consumption (including reduction, sorptions, and desorptions) and the temperature of the reactor were measured simultaneously by a TCD-GC and a thermocouple, respectively. After a stable TCD (thermal conductivity detector) baseline had been reached, the reactor was warmed to room temperature to start the reduction reaction. After being held at room temperature for a while, the reactor was heated to a determined plateau temper-

ature by a temperature programmer in order to desorb the sorbed hydrogen; it was then cooled to room temperature for hydrogen sorptions. This treatment of heating to an elevated plateau temperature and cooling to room temperature was usually performed many times on any given sample in order to study the variation of the sorption phenomena with the temperature of hydrogen treatment.

RESULTS AND DISCUSSION

Figure 1 is an illustrative TPR-TRS ex-

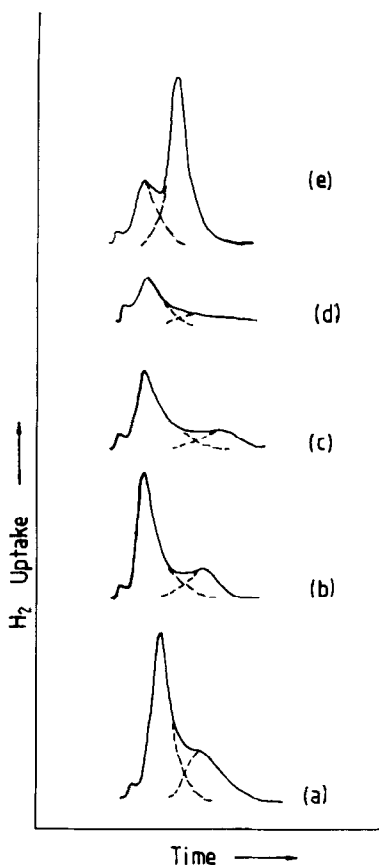


FIG. 2. Consecutive TRS spectra of a Pd/TiO_2 sample. Overlapped hydrogen chemisorption and absorption peaks are resolved with dotted lines. The plateau H_2 desorption temperatures for the TRS spectra of a, b, c, and d are 350, 450, 500, and 575°C , respectively. The sample was then calcined at 400°C in air to relieve the SMSI state. Profile e was the resulting TRS spectrum after reducing the calcined sample in the H_2/Ar stream at 350°C .

periment on precalcined (400°C) Pd/SiO₂ (Sample A). After warming to room temperature in the H₂/Ar gas stream, two cycles of heating to 400°C and cooling to room temperature were performed. Desorption of hydrogen from palladium in the heating phase of the second temperature cycle was found to proceed in two steps. Absorbed hydrogen desorbed around 90°C while chemisorbed hydrogen desorbed at higher temperatures. Palladium resorbs hydrogen in the cooling phase of these two temperature cycles. No difference was found between the TRS spectra obtained. The palladium in this sample should have been at the same dispersion when these two TRS spectra were taken. Pd/SiO₂ is therefore a fairly stable catalyst in the hydrogen environment at 400°C.

Figure 2 shows a series of TRS results for 0.82 g of sample B (Pd/TiO₂) after various TPR treatments. Profile a is the TRS spectrum after a TPR with the plateau tempera-

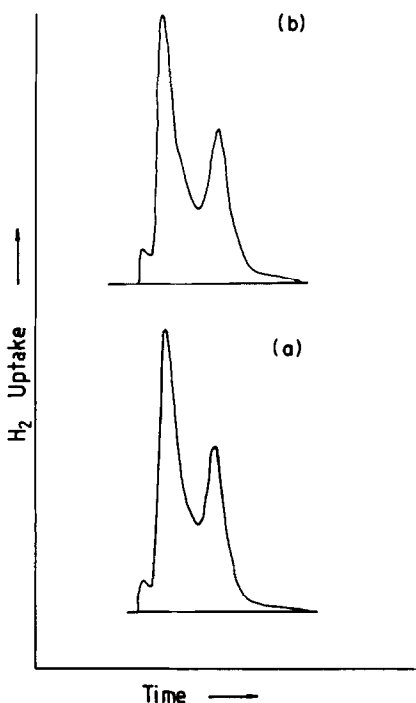


FIG. 3. Consecutive TRS spectra of a Pd/SiO₂ sample with the plateau heating temperature at (a) 400°C and (b) 600°C, respectively.

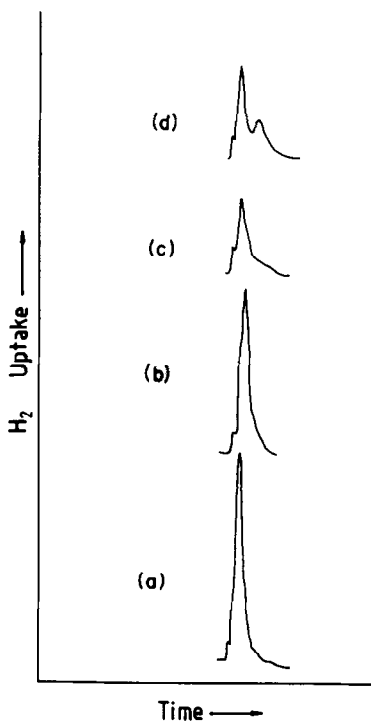


FIG. 4. Consecutive TRS spectra of a Pd/Al₂O₃ sample with the plateau heating temperature at 400, 600, and 800°C (a–c). The sample was then subjected to a 400°C calcination. Spectrum d is the TRS spectrum after the calcination and a TPR to 400°C.

ture at 350°C. This profile consists of two overlapping peaks. The first peak comes from the hydrogen chemisorption and the second (a shoulder) results from the absorption. This sorption profile indicates a 40% dispersion of palladium metal according to Eq. (1). This sample was subsequently heated in the H₂-Ar gaseous stream to higher plateau temperatures and a TRS was recorded on cooling the sample back to room temperature (25°C) after each reduction. The uptake of hydrogen in the TRS decreases with the increasing of the reduction temperature (profiles b to d). This suppression of H₂ uptake (the sorption area of d was reduced to less than one quarter of the area of a) is consistent with the reported tendency of TiO₂ to establish SMSI with supported metals under severe reduction conditions. Profile e further confirms that

the SMSI state may be destroyed by 400°C oxidation. Upon this oxidation treatment and a moderate reduction, palladium resumes its capacity for H₂ uptake. However, the dispersion of the palladium defined by Eq. (1) was found to decrease from 40 to 15% due to the series of reduction and oxidation treatments.

Tauster *et al.* (2) have proposed that SMSI was possibly caused by an electron flow from reduced cations to supported metals. Theoretically, extra electrons on surface metal atoms may induce a decrease in the binding energy of their ESCA spectra. However, experimental results did not indicate any binding energy shift from supported metals under SMSI states (6, 7). An increase of electron density on surface atoms by SMSI may also be detected from infrared spectroscopy. According to coordination chemistry, the vibrational frequency of CO attached to metal atoms reflects the electron density of the atoms (the higher the electronic density on the metal the lower the CO stretching frequency) (8).

Vannice *et al.* (9) studied Pt/Al₂O₃ catalysts using IR and found that the stretching frequency of chemisorbed CO was actually slightly increased under SMSI conditions. Negligible electron transfer from reduced cations of supports to dispersed metal atoms on SMSI is therefore indicated by both ESCA and IR studies.

The TRS spectra of Fig. 2 reveal the variation of H₂ sorption with reducing temperature. SMSI suppresses not only the chemisorption but also the absorption. Interdiffusion of reduced support cations with dispersed metals (10, 11) and alloy formation (such as Pt-Al (12) and Ni-Si (13)) have been suggested in the literature as the reason for SMSI. The present experimental result may be explained by the diffusion of partially reduced TiO₂ to the palladium surface. On calcination, reduced titanium ions (probably at +3 oxidation state) oxidized to TiO₂ and aggregated into large particles.

Alumina and silica are two of the most important supports for metallic catalysts. Figure 3 compares the TRS spectra of Pd/

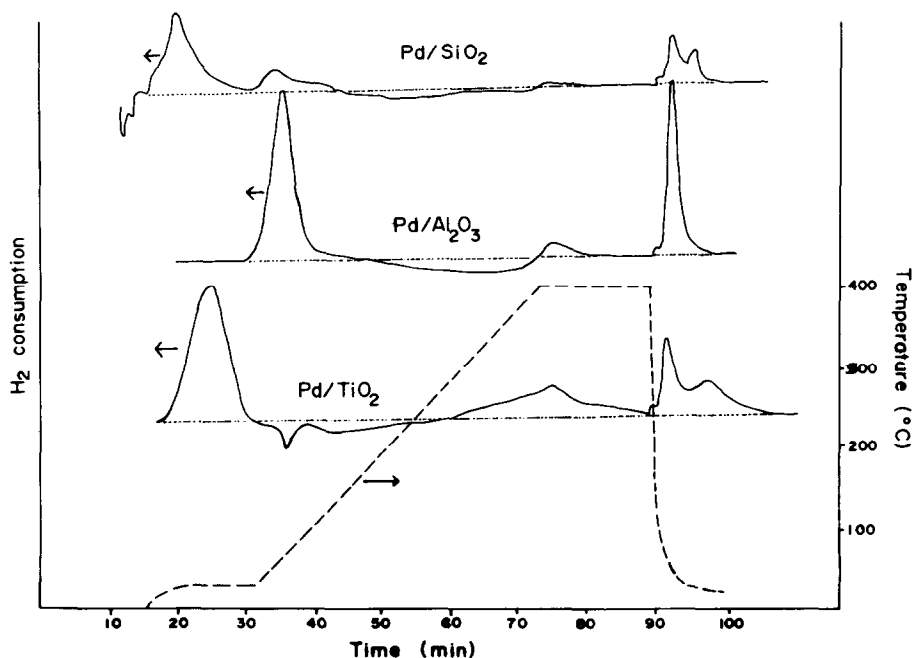


FIG. 5. TPR-TRS spectra for supported Pd catalysts of various oxides. The dashed line indicates the temperature profile. Dotted lines are the expected baselines.

SiO₂ (sample A) reduced at 400 and 600°C. Negligible SMSI was found for this sample after a 8 h reduction treatment at 600°C. Pd/Al₂O₃ (sample C), however, did show a small degree of SMSI under 600°C reduction. Again, the SMSI state of this sample may be removed by a calcination at 400°C (see Fig. 4). In contrast to Pd/TiO₂, Pd/Al₂O₃ remained at modest dispersion under the severe reduction (800°C) and calcination (400°C) conditions. The small peak area of Fig. 4d on comparing with that of Fig. 4a may indicate that some reduced support materials blocked the surface of the metal crystallites in the high-temperature reduction. This blockage was partially recovered in the calcination.

The tendency for SMSI formation between dispersed palladium and supports is therefore increased in the following order:



This order may be correlated with the TPR spectra (Fig. 5) of these catalysts. H₂ desorption is seen to start at moderate temperatures (around 60°C). The extent of this desorption increases with the reactor temperature. Negligible H₂ consumption is found for Pd/SiO₂ after the plateau temperature (400°C) is reached. A small hump, however, is found for Pd/Al₂O₃ at the beginning of this plateau, indicating that a hydrogen consumption process occurred at this temperature. This hydrogen may be consumed by a spillover from palladium to Al₂O₃. The spillover of hydrogen to TiO₂ becomes extensive in Fig. 5 at temperatures less than 300°C. The reducibility of TiO₂ is therefore much higher than that of Al₂O₃ and SiO₂. Tauster *et al.* (2) have correlated the SMSI behavior observed from chemisorption with the thermodynamic reducibility of supports. The present TPR and TRS system can give an experimental relationship between the extent of support reduction and the SMSI effect simultaneously.

The change in the TRS spectra with pla-

teau temperature is interesting for Pd/C (sample D). The peak of H₂ absorption gradually increases at the expense of that of H₂ chemisorption on increasing the plateau temperature from 150 to 500°C (Figs. 6a–e). Profile e reveals that the chemisorption ability cannot be restored by a calcination treatment. SMSI, therefore, plays a negligible role on the Pd/C sample. Sintering is the major consequence from the high-temperature treatment in the H₂ environment.

In summary, TPR is a useful technique to study the reduction of calcined metallic catalysts and the spillover of hydrogen from

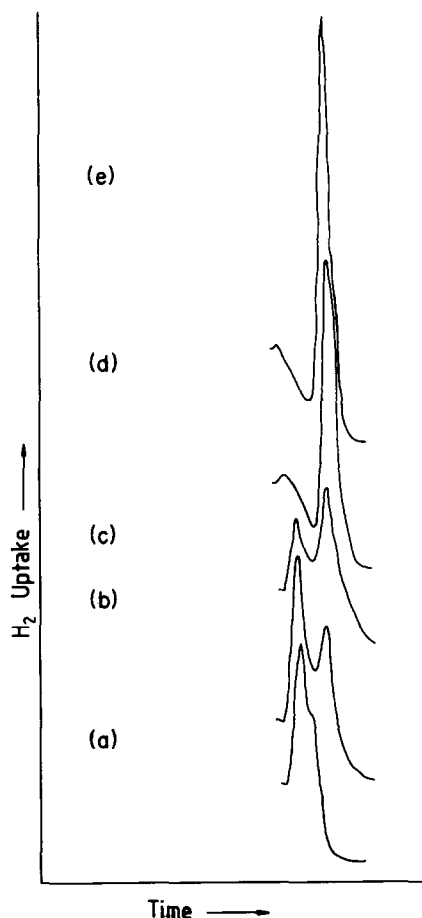
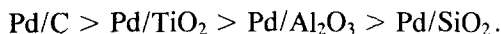


FIG. 6. Consecutive TRS spectra on a Pd/C sample with the plateau temperature at 150, 300, 400, and 500°C (profiles a–d). Profile e is the TRS spectrum after a subsequent 200°C calcination and a TPR to 300°C.

reduced metal to supports. Metallic catalysts are prone to sinter under elevated temperatures in the H₂ environment. A reduction to the metallic form by hydrogen, however, is an inevitable part of the pre-treatment routine for studies of chemisorption in order to determine the dispersion of metallic catalysts. The TPR technique gives information on the minimum temperature that can completely reduce the metal crystallites in the catalysts without causing serious sintering. A study of TPR also helps to prevent SMSI states that may suppress the chemisorption ability of catalysts. Finally, we think the feasibility of supported metal crystallites to sinter depends on the supports. This study found the following trend



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